Phosphorus Transport in Overland Flow in Response to Position of Manure Application

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ABSTRACT

Phosphorus (P) loss in overland flow varies with spatial distribution of soil P, management, and hydrological pathways. The effect of flow time, flowpath length, and manure position on P loss in overland flow from two central Pennsylvania soils packed in boxes of varying length (0.5, 1.0, 1.5, 2.75, and 4.0 m long × 15 cm wide × 5 cm deep) were examined by collecting flow samples at 5-min intervals for 30 min (50 mm h^{-1} rainfall) without and with 75 kg P ha^{-1} applied as swine (*Sus scrofa*) manure over 0.5 m of the box slope length at distances of 0 to 3.5 m from the downslope collection point. Dissolved reactive P concentration was more closely related to the proportion of clay in sediment of overland flow before ($r = 0.98$) than after ($r = 0.56$) manure application. This was attributed to the transport of larger, low-density particles after applying manure. The concentration of dissolved and particulate P fractions decreased with increasing flowpath length, due to dilution rather than sorption of P by surface soil during overland flow. Total P loss (mainly as particulate P) from the Watson channery silt loam (fine-loamy, mixed, active, mesic Typic Fragiudult) was more than from Berks channery silt loam (loamy-skeletal, mixed, active, mesic Typic Dystrudept), even with manure applied. Thus, while P loss in overland flow is affected by where manure is applied relative to flowpath length, initial soil P concentration should not be discounted when looking at areas of potential P loss within a watershed.

P HOSPHORUS is a key element in the nutrition of plants and the eutrophication of surface waters. The loss of P from soil to surface waters is mediated by the hydrological conditions controlling water flow (e.g., overland and subsurface flow) and can occur in both dissolved and particulate forms. Particulate phosphorus (PP) is usually defined as P that does not pass a 0.45-μm filter. In the continental climate of the northeastern USA, most P is lost via overland pathways (Pionke et al., 1999). From cultivated land, PP can account for 75 to 90% of the total P transported (Sharpley and Reko-lainen, 1997).

The potential loss of P in different forms during overland flow is a function of erosion, soil P concentration, and management. Sharpley (1985a) described the concentrations of dissolved phosphorus in overland flow by a function that related soil volume and surface soil P concentration to the power of soil constituent concentrations (e.g., soil P, clay, and organic C content). Essentially, the power function describes a quantity–intensity relationship, where the eventual dissolved P concentration (intensity) of overland flow is related to the concentration (quantity) of P in the soil. Recent work showed that this relationship varies with soil types and management conditions (McDowell and Sharpley, 2001a; Mc-

Dowell et al., 2001a). The nature of the erosion process means that finer-sized particles, which also contain much more P than coarser-sized particles, are eroded first. However, the concentration of P in water in equilibrium with fine particles can be much less (relative to the total concentration of P in the particle) than from coarse particles (Maguire et al., 1998).

Once P is in solution, the transition between dissolved and particulate forms during overland flow can change, mediated by sorption–desorption properties of the sediments. However, the majority of processes have been examined in reference to fluvial systems and in response to point additions of P (House et al., 1995). Consequently, soil landscape position can profoundly affect the concentration of P lost, a process not presently well understood.

We hypothesize that if a recently manured soil is far enough upslope, the concentration of P in overland flow may decrease to less than that required to cause eutrophication by the time flow reaches surface water. The purpose of this paper is to examine processes and fractions of P within overland flow, with and without a localized manure application, at various distances upslope for two soils that dominate a watershed in central Pennsylvania, USA. Previous work has shown that physical transport mechanisms and sources of P within this watershed are controlled largely by landscape position (McDowell et al., 2001b). Thus, a secondary objective was to estimate where from within our watershed manured soils would affect P export.

MATERIALS AND METHODS

Soils

Soil samples (0–5 cm) were taken from each of two soil types (one representing low, and one high soil P concentration) at two sites within FD-36, a 39.5-ha subwatershed of Mahantango Creek. The creek is a tributary of the Susquehanna River and ultimately the Chesapeake Bay. The soils are Berks (330 g kg^{-1} clay and 26 g kg^{-1} total C) and Watson (390 g kg^{-1} clay and 17 g kg^{-1} total C) channery silt loams from cultivated fields [permanent arable, cultivated from soybean, *Glycine max* (L.) Merr.] that have received different fertilizer and manure (largely swine) inputs over the last 10 to 15 yr. These two soils (of different soil P concentrations) were taken from areas likely to contribute overland flow to stream flow and they represent ca. 80 and 20% of textural classes within the watershed (Gburek et al., 2000; McDowell et al., 2001b).

Boxes and Manure Application

The four soils were air-dried, sieved (<6 mm), poured, and packed (by shaking and placing pressure on the soil surface

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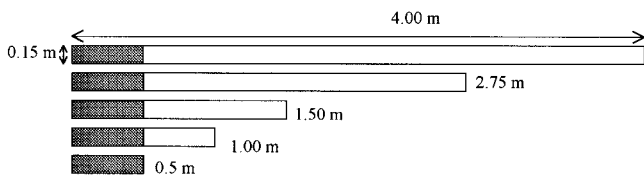
Fig. 1. Relative manure application to each soil box (to scale). Downslope is at the right-hand end for each box.

with a board) into five impermeable boxes (plastic lined and constructed of plywood) of varying length (Fig. 1) to a bulk density of 1.1 g cm^{-3} (representative of field conditions). Overland flow was generated by applying artificial rainfall (tap water, P less than detection limit of 0.005 mg P L^{-1}) at 50 mm h^{-1} for 30 min to each boxed soil, inclined at 5% slope. All rainfall was produced with size, velocity, and impact angles approximating natural rainfall (Shelton et al., 1985). Samples were taken five times for every 5 min of overland flow.

After the control event (unmanured soil), soils were replaced with new soil and swine manure applied to the surface of the first 0.5 m of each box at a N-based rate of ca. 200 kg N ha^{-1} equivalent to 75 kg P ha^{-1} (Sharpley and Beegle, 1999; Fig. 1). The swine manure used had a total P concentration of 33.0 g kg^{-1}, inorganic P of 30.1 g kg^{-1}, organic P of 2.5 g kg^{-1}, water-soluble P of 6.1 g kg^{-1}, organic C of 260 g kg^{-1}, and pH of 7.3 (Sharpley and Moyer, 2000). After a period of 1 wk, during which time the manure was allowed to dry and equilibrate with the soil, overland flow and sampling was then repeated as described above. All treatments were duplicated.

The rainfall simulation and packed soil boxes used in this study were designed to study interactions between surface soil and overland flow water and mechanisms controlling the release of soil P to overland flow (Sharpley, 1985b, 1995; Sharpley et al., 1981a). Although these boxes were found to accurately represent field processes, and as such mimic processes involved in saturation-excess overland flow, they are not designed to quantify field losses of P per se (Sharpley et al., 1982, 1988).

Soil, Runoff, and Drainage Water Analyses

Prior to overland flow generation, triplicate subsamples of soil were taken for analysis of Mehlich-3 extractable P (Mehlich, 1984). Soil samples were collected during box packing for unmanured soil. For manured soils, a 2-cm-deep sample was collected from the upslope end of the box to minimize any effects on overland flow. Water-extractable P was also determined in triplicate using the mean sediment to solution ratio of overland flow (1 g to 350 mL for the Berks soil and 1 g to 100 mL for the Watson soil). For each water extraction, soil was shaken for 30 min before the suspension was filtered (<0.45 μm) and P determined colorimetrically (Murphy and Riley, 1962).

Overland flow samples, collected at 5-min intervals after the onset of flow (to the 30 min mark), were filtered (<0.45 μm) and stored at 4°C in the dark along with unfiltered samples. Within 24 h, each sample was analyzed for dissolved reactive phosphorus (DRP) and within 48 h for total dissolved reactive phosphorus (TDP) after a Kjeldahl digestion (Bremner and Mulvaney, 1982). An unfiltered sample was also digested and total P (TP) measured within 7 d. Dissolved unreactive phosphorus (DURP) was defined as the difference between TDP and DRP and particulate P as TP less TDP, respectively.

Suspended sediment from each overland flow sample was collected after 7 d, by centrifuging (2600 × g), removing the supernatant, and air-drying the residue. Selected sediment

samples (of weight > 3 g) were analyzed for their particle size distribution (undispersed) using the pipette method with and without prior oxidation with hydrogen peroxide to remove organic matter (Gee and Bauder, 1986). Mehlich-3 extractable P and water-extractable P (using the method outlined above) were determined on the sediment samples (Mehlich, 1984).

Statistical Analyses

Data were analyzed (one-way analysis of variance, curve fits, constants, correlation coefficients, and levels of significance) using SPSS v10.0 (SPSS, 1999). In all cases where P fractions were plotted against time or flowpath length, data were fitted to a power equation ($y = ax^b$; where y is the P fraction and x is time or area and a and b are constants). Data are presented as the mean of duplicates. Statistical comparisons of soil type and treatment effects on P transport in overland flow were made using significant regression parameter fits. Due to the limited number of degrees of freedom, no effort was made to compare individual samples among treatments.

RESULTS AND DISCUSSION

Soil and Sediment Phosphorus Characteristics

Data for soil-extractable P concentrations and corresponding enrichment ratios before and after manure application are given in Table 1 for soil, and the sediments derived from them, during overland flow. As expected, soils that received manure exhibited much greater Mehlich-3 and water-extractable P concentrations than those that were unmanured. However, compared with the enrichment ratios of Mehlich-3 extractable P, ratios of water-extractable P increased much more in the Berks and Watson soils possessing greater initial Mehlich-3 extractable P concentration. This effect is well documented and can be attributed to the nonlinear quantity–intensity relationship between the two measures of soil P (McDowell et al., 2001a). Indeed, McDowell and Sharpley (2001a,b) found that the potential for P loss is much greater in excess of ca. 190 mg kg^{-1} Mehlich-3 extractable P for the Berks soil and 240 mg kg^{-1} Mehlich-3 extractable P for the Watson soil.

Similar to the soils, enrichment ratios for Mehlich-3 extractable P in sediments from the manured soil compared with unmanured soil were greater in those soils of greater initial P concentration (Table 1). However, the magnitude of enrichment ratios was significantly greater ($P < 0.05$) in the sediments compared with the soils. This is a well-known and documented phenomenon and has been explained in the past by the selective erosion by overland flow of fine particles that contain a much greater concentration of P compared with the whole soil (Sharpley, 1980a, 1985a). However, the comparable enrichment ratios for water-extractable P from sediments were not significantly different from the enrichment ratio of the soils ($P > 0.05$). This implies that the water solubility of P derived from selectively eroded fine sediments is not as great as that in whole soil. In fact, Maguire et al. (1998) reported similar findings from soils fractionated into different particle sizes. While fine sediments may contain a greater proportion of Mehlich-3 extractable P compared with coarser sediments,

Table 1. Mean soil and sediment P quantity and intensity measures and enrichment ratios (ER). Numbers in parentheses represent the standard error of the mean.

Soil or sediment	Mehlich-3 extractable P	Water-extractable P	ER of manured to unmanured	
			Mehlich-3	Water
	mg kg^{-1}	mg L^{-1}		
Soils				
Manured				
Berks low P	255 (21.7)	0.30 (0.01)		
Berks high P	346 (8.4)	0.37 (0.04)		
Watson low P	131 (1.1)	0.51 (0.01)		
Watson high P	396 (32.3)	1.35 (0.06)		
Unmanured				
Berks low P	134 (2.4)	0.12 (0.01)	1.90	2.42
Berks high P	225 (4.7)	0.13 (0.01)	1.53	2.93
Watson low P	67 (2.4)	0.21 (0.01)	1.97	2.44
Watson high P	264 (14.2)	0.86 (0.03)	1.50	1.56
Sediments				
Manured				
Berks low P	881 (150.0)	0.71 (0.03)		
Berks high P	901 (119.6)	1.89 (0.18)		
Watson low P	443 (49.2)	0.34 (0.08)		
Watson high P	548 (117.0)	0.35 (0.01)		
Unmanured				
Berks low P	252 (15.7)	0.29 (0.04)	3.49	2.45
Berks high P	558 (63.1)	0.72 (0.08)	1.61	2.62
Watson low P	124 (30.8)	0.09 (0.02)	3.57	3.77
Watson high P	405 (37.3)	0.26 (0.01)	1.35	1.35

water-extractable P is greater in coarse than fine sediments.

Measurements of suspended sediment were not significantly different between low and high P soils, but the Watson soil eroded at a rate three and a half times that of the Berks soil (mean sediment to solution ratios of 1:100 and 1:350, respectively; different at the $P < 0.01$ level [data not shown]). Sediment samples collected during overland flow were extracted at the mean sediment to solution ratios approximating those expressed in situ. This may more accurately reflect the cation status and ionic strength of the aqueous phase of the surface soil and is more likely to estimate DRP in overland flow than an unrealistic ratio (Beauchemin et al., 1996; McDowell and Sharpley, 2001a; Ryden et al., 1972a,b). Indeed, a regression equation for DRP in overland flow against water-extractable P showed a highly significant relationship that was also of a similar magnitude as concentration (i.e., slope near to 1). For the Berks soil, this was described by DRP = 0.733 × water-extractable P + 0.0389, $r^2 = 0.591$** ($n = 16$); and for the Watson soil by DRP = 1.07 × water-extractable P + 0.0006, $r^2 = 0.903$*** ($n = 28$).

Kinetic Variation of Phosphorus Fractions

Parameters for the significance of a power equation ($y = ax^b$) fitted to data for P fractions at each overland flow collection time in untreated soils are given in Table 2. No significant fit could be found between P fractions and time following manure application except for the Berks low P soil (DURP = $7.960x^{-0.88}$, $P < 0.05$) and Berks high P soil (DURP = $0.036x^{1.26}$, $P < 0.05$).

The parameters in Table 2 indicate that for all fractions except DURP, concentration decreases with time after onset of overland flow. For brevity, we can use constant a as an indication of the relative concentration of P fraction and constant b as an indicator of the relative curvature with, in this case, time and later flowpath length. An example of the behavior of P fractions in the Berks high P and Watson low P soil is given in Fig. 2. As expected, PP makes up the majority of TP in all soils (Fig. 2, Table 2). However, in the manure-treated soils (Fig. 3, Table 3), dissolved fractions (DRP and DURP) constitute nearly half of TP, due to the influence and greater solubility of P in manure than in soil.

The decrease of DRP (Fig. 3) with time has been noted in previous studies. For example, Sharpley (1980b)

Table 2. Parameters and significance of fit of the power function between P fractions and time (min; x) for each duplicated, untreated soil.

P fraction†	Berks		Watson	
	Low P	High P	Low P	High P
DRP	$0.530x^{-0.18}$***	$0.263x^{-0.05}$***	$0.161x^{-0.08}$*	$1.234x^{-0.33}$***
DURP	$0.015x^{0.93}$**	$0.049x^{0.38}$*	$0.025x^{0.48}$*	ns
TDP	ns‡	ns	$0.154x^{0.15}$*	$2.224x^{-0.44}$***
PP	$12.505x^{-0.28}$**	$6.070x^{-0.15}$**	ns	$18.370x^{-0.26}$*
TP	$12.539x^{-0.25}$**	$6.242x^{-0.13}$**	ns	$20.410x^{-0.27}$*

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
† DRP, dissolved reactive phosphorus; DURP, dissolved unreactive phosphorus; TDP, total dissolved reactive phosphorus; PP, particulate phosphorus; TP, total phosphorus.
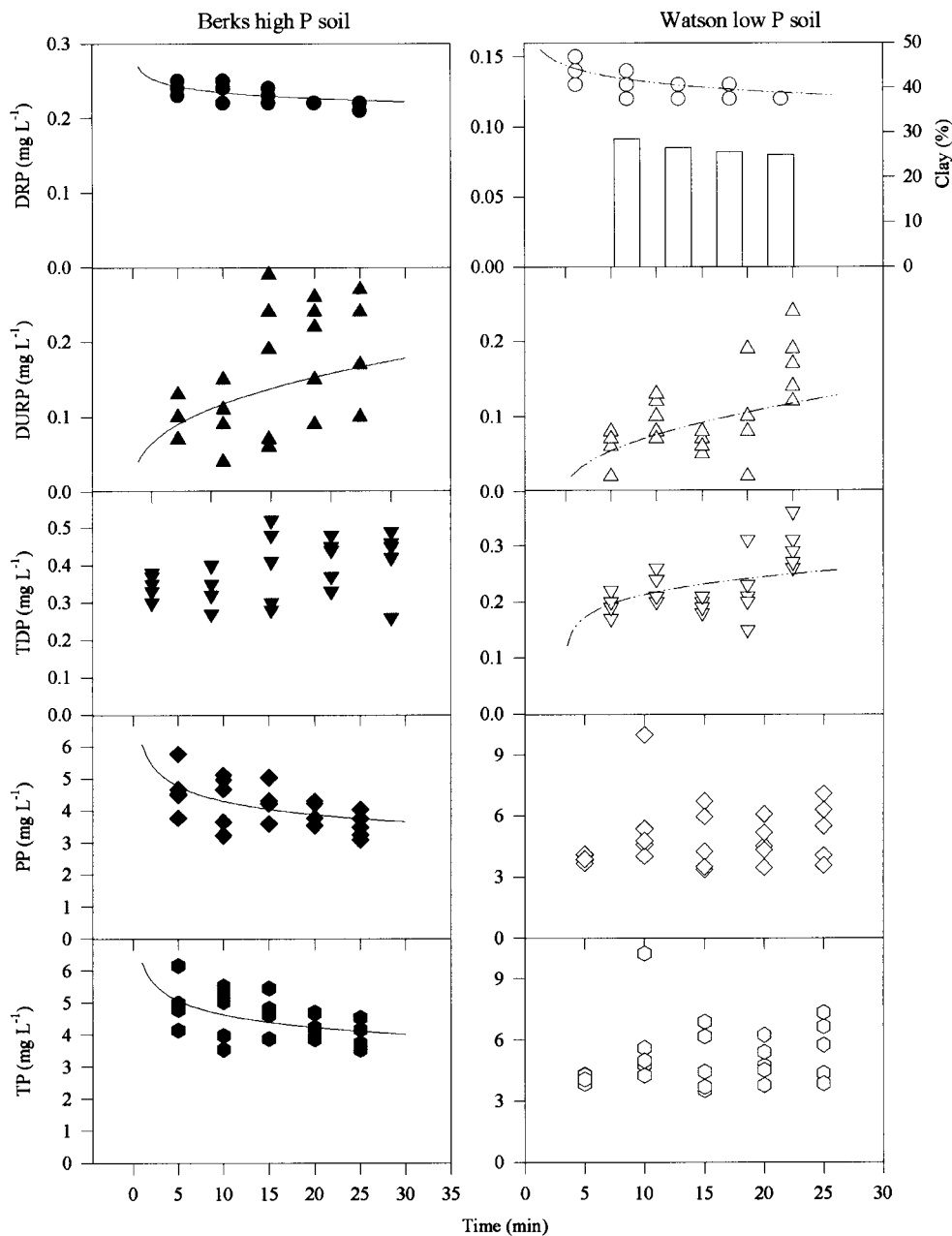‡ ns = not significant.

Fig. 2. Variation of P fractions with time for untreated Berks high P and Watson low P soils. Lines represent the fit of the power equation to the data. No line represents a nonsignificant fit. Vertical bars represent the percent clay in each sediment sample. DRP, dissolved reactive phosphorus; DURP, dissolved unreactive phosphorus; TDP, total dissolved reactive phosphorus; PP, particulate phosphorus; TP, total phosphorus.

attributed a 50% decrease in DRP concentrations with time to the dilution of soil solution. While this may generally be the case, especially in systems where little sediment is transported in overland flow, it is an oversimplification because erosion processes are also involved. The rate of erosion of sediments during a rainfall event decreases with time. Stoltenberg and White (1953) attributed this to the selective removal of fine material from the soil surface, which results in a crust or "pavement" at the surface of the coarser and/or denser material left behind.

Unless the kinetic energy (intensity) of rainfall increases, erosion of coarser materials is unlikely to occur.

Figure 2 represents an example of the decrease in finer particles in the untreated Watson low P soil. In addition, Table 4 shows that the proportion of clay-sized sediments of Berks low P sediment is positively correlated to Mehlich-3 extractable P and DRP concentrations. As for the whole sediments, the correlation is better with water-extractable P than with Mehlich-3 extractable P due to the nonlinear quantity–intensity relationship that exists between them (McDowell and Sharpley, 2001a).

Beuselinck et al. (2000) noted that large aggregates of low density are easily transported by rolling over the bed as flocs. In addition, Barthés et al. (1999, 2000) noted a negative relationship between field-scale ero-

Table 3. Parameters and significance of fit for the power function between P fractions and flowpath length (m; x) for each duplicated, treated soil.
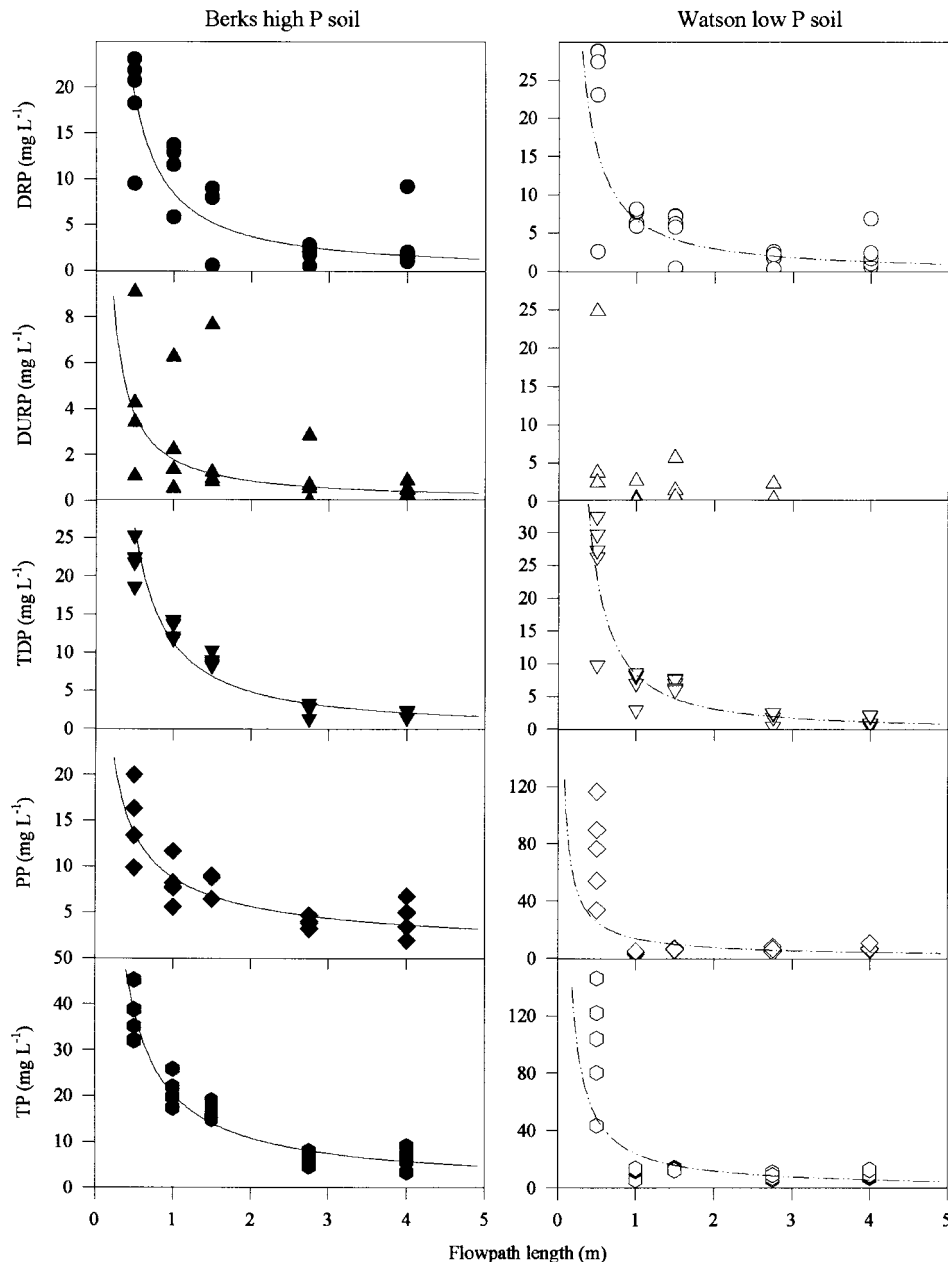
| | Berks | | Watson | |
P fraction†	Low P	High P	Low P	High P
DRP	$9.78x^{-0.88}$***	$8.44x^{-1.18}$***	$6.71x^{-1.21}$***	$8.19x^{-0.93}$***
DURP	$1.18x^{-0.85}$**	$1.79x^{-1.06}$**	ns‡	ns
TDP	$11.70x^{-0.90}$***	$11.29x^{-1.22}$***	$8.36x^{-1.46}$***	$9.46x^{-1.07}$***
PP	$17.02x^{-1.18}$**	$8.76x^{-0.64}$***	$13.88x^{-0.87}$**	$21.21x^{-0.72}$**
TP	$30.39x^{-1.11}$***	$20.44x^{-0.92}$***	$23.98x^{-1.03}$***	$33.78x^{-0.83}$***

** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
† DRP, dissolved reactive phosphorus; DURP, dissolved unreactive phosphorus; TDP, total dissolved reactive phosphorus; PP, particulate phosphorus; TP, total phosphorus.
‡ ns = not significant.

Fig. 3. Variation of P fractions with flowpath length for treated Berks high P and Watson low P soils. Lines represent the fit of the power equation to the data. No line represents a nonsignificant fit. DRP, dissolved reactive phosphorus; DURP, dissolved unreactive phosphorus; TDP, total dissolved reactive phosphorus; PP, particulate phosphorus; TP, total phosphorus.

sion in overland flow and topsoil aggregate stability and organic carbon concentration. Hence, in the current study, it is possible that manure application may have influenced the erosion of sediments. This is evident from Table 4, where the correlation of Mehlich-3 extractable P to eroded sand-sized particles is stronger in manured sediments than in sediments from unmanured soils. We can infer from this that manure application resulted in increased loss and importance of larger, lower density particles (possibly as flocs of small and large particles) during overland flow by simply rolling over the surface.

Perhaps the most important factor increasing erosion from untreated soil is slaking and dispersion, which occurs during the wetting of dry soil. Soils with little organic matter (e.g., many arable soils) are particularly prone to these processes. Slaking occurs when unequal pressures of entrapped air and the differential swelling of clays cause aggregate decomposition. If the hydration–osmotic forces within microaggregates are sufficient to overcome the attractive forces between them, clay platelets (<2 μm) may disperse (Kemper and Rosenau, 1984; Dickson et al., 1991; Haynes, 1993). Haynes and Swift (1990) and Haynes (1993) found that in soils sampled from long-term arable sites, the proportion of water-stable aggregates declined until a near-constant value was reached; a trend mimicked here by the decrease in most P fractions with time since the start of overland flow.

In our study, the importance of aggregation and its controlling effect on P fractions can be seen by comparing the untreated eroded sediments with and without oxidative treatment to remove organic matter (Table 4). The fact that particle size fractions, and especially clay-sized particles within the untreated eroded sediments, are better correlated to DRP concentrations than to H_2O_2 treated eroded sediments suggests that slaking, dispersion, and organic matter (for the creation of flocs and presumably derived from manure) are important factors in P dynamics during an overland flow event.

Variation with Flowpath Length

Changes in concentration of each P fraction in overland flow in response to a localized manure application covering 0.5 m of flowpath lengths varying from 0.5 to 4.0 m (100% to 12.5% of total flowpath length) are given in Table 5. The data (an example of which is given in Fig. 3) show that P concentrations of all fractions decreased with increasing flowpath length (negative power function). However, changes in DURP were not significant in two of the soils. In contrast to the unmanured soils, no significant relationship was found for the variation of most P fractions with time, indicating that during the 30 min of overland flow, the effect of slaking and/or dispersion was overshadowed (or minimized by manure

Table 4. Correlation coefficients for the relationship between the percentage sand, silt, and clay to Mehlich-3 extractable P in sediments or dissolved reactive phosphorus (DRP) in overland flow.

Soil	Mehlich-3 extractable P			DRP in overland flow		
	Sand†	Silt	Clay	Sand	Silt	Clay
H_2O_2 treated						
Berks low P	0.081	0.327	0.421	0.221	0.030	−0.439
Watson low P	−0.688**	0.342	0.452	−0.351	0.503	0.024
Watson high P	−0.236	0.130	0.050	−0.377	0.030	0.308
Untreated and unmanured						
Berks low P‡	−0.719*	0.407	0.985***	−0.765**	0.889***	0.979***
Watson low P	0.687**	0.219	0.275	−0.574*	−0.248	0.345
Watson high P	0.297	0.133	−0.387	−0.314	−0.060	0.551*
Manured						
Berks low P	0.541*	0.212	−0.387	−0.985***	0.598*	0.559*
Watson low P	0.809**	−0.263	−0.053	0.562*	−0.110	0.165
Watson high P	0.709**	0.071	−0.401	−0.616*	0.232	0.724**

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
† Size fractions refer to >63 μm for sand, between 63 and 2 μm for silt, and <2 μm for clay. However, note that in all samples except those treated with H_2O_2 these elucidate the behavior of each size classification in water and do not refer to true clay, silt, or sand particles.
‡ No data were available for the Berks high P soil as not enough sediment samples of sufficient weight (>3 g) were available for particle size fractionation.

Table 5. Parameters and significance of fit for the power function between P fractions and flowpath length (m; x) for the difference between duplicated, treated, and untreated soil.

P fraction†	Berks		Watson	
	Low P	High P	Low P	High P
DRP	$9.28x^{-0.73}$***	$7.63x^{-1.25}$***	$6.16x^{-1.26}$***	$6.36x^{-1.00}$**
DURP	$0.99x^{-1.14}$**	$1.74x^{-1.02}$**	$1.80x^{-1.30}$*	ns‡
TDP	$10.84x^{-0.78}$***	$10.20x^{-1.27}$***	$7.37x^{-1.50}$***	$7.21x^{-1.26}$***
PP	$11.91x^{-1.51}$*	$4.09x^{-1.39}$***	$5.89x^{-1.25}$**	$18.92x^{-1.36}$***
TP	$15.23x^{-1.07}$*	$13.99x^{-1.71}$***	$17.00x^{-1.47}$***	$16.00x^{-1.12}$***

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
† DRP, dissolved reactive phosphorus; DURP, dissolved unreactive phosphorus; TDP, total dissolved reactive phosphorus; PP, particulate phosphorus; TP, total phosphorus.
‡ ns = not significant.

application) and that the supply of each P fraction was not decreasing.

To account for effects of slaking and dispersion, which occurred in the untreated soil, data for P fractions in manured soils were subtracted from the accompanying data for unmanured soils, yielding just the effect of manure on P overland flow dynamics. An example of the data for two soils is given in Fig. 4 and the parameters of fit for all data are given in Table 5. The similarity of data in Table 5 and Fig. 4 to data in Table 3 and Fig. 3 suggests that localized manure application is the predominant factor influencing P fractions in overland flow.

Isolating the effect of manure also revealed a signifi-

cant effect of time on DURP in the Berks soils (Berks low P soil, DURP = $12.24x^{-1.17*}$ and Berks high P soil, DURP = $0.014x^{1.61**}$), which could reflect the different ratio of inorganic P to organic P in manure and the soil or the greater mobility of organic P (included within DURP) compared with DRP in overland flow. Frossard et al. (1989) showed that organic P forms were much more soluble in soil solution and mobile in soil than orthophosphate. Similarly, Chardon et al. (1997) found that the application of swine manure containing 46% inorganic P for 12 yr had enriched soil solution at 70 to 80 cm deep, to yield 90% dissolved organic P compared with 10% at the soil surface.
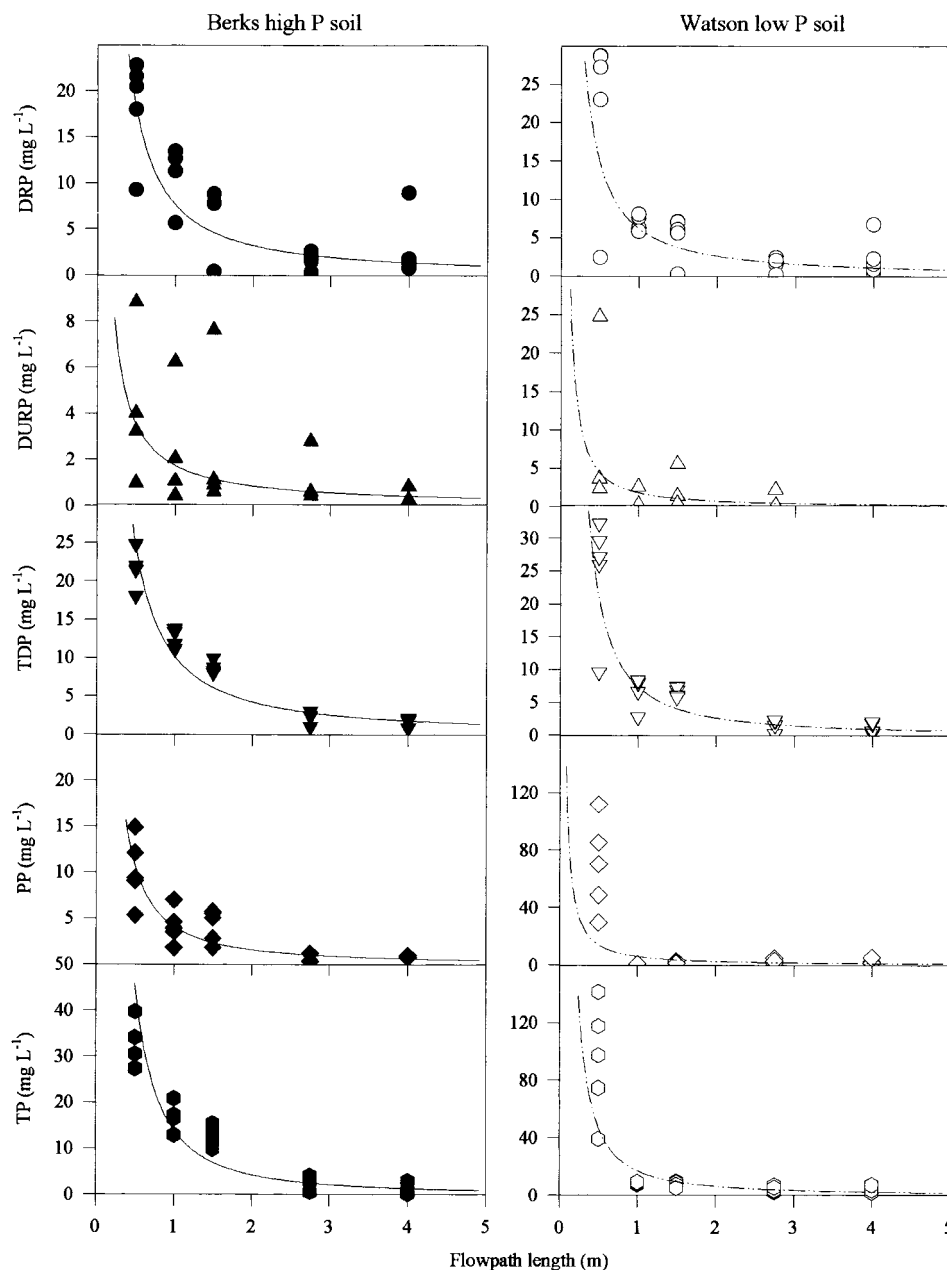

Fig. 4. Variation of P fractions with flowpath length for the difference between manured and untreated Berks high P and Watson low P soils. Lines represent the fit of the power equation to the data. DRP, dissolved reactive phosphorus; DURP, dissolved unreactive phosphorus; TDP, total dissolved reactive phosphorus; PP, particulate phosphorus; TP, total phosphorus.

From Fig. 4 it is evident that the two soils differ greatly in their P loss potential, the Watson soil having a far greater potential loss of total P than the Berks soil. Both chemical and physical characteristics of the soils and the interaction of the manure can explain the difference. For example, the clay fraction of soil contains the majority of the sorbed P, and the Watson soil contains more clay than the Berks soil (39% and 33%, respectively; McDowell et al., 2001b). When clay is selectively eroded, the Watson soil should lose P at a greater rate than the Berks. However, perhaps of more importance are the physical characteristics of the two soils. The Berks soil has an infiltration capacity four times that of the Watson soil (ca. 5.0 and 1.25 cm h^{-1}, respectively; Eckenrode, 1985), and while both received the same volume of water and manure, the Berks soil would have allowed more infiltration to occur. Consequently, while the Watson soil may have been "caked" by manure settling on the surface, more manure would have soaked into the Berks soil and been less available for transport in overland flow. This effect is indicated in Fig. 4 by the much greater scatter of points at the 0.5-m flowpath length in the Watson soil compared with the Berks soil.

A uniform decrease in P fractions with flowpath length indicates that the major factor influencing the concentration of P in overland flow is that of dilution by overland flow over the unmanured lengths of soil (varying from 50 to 88% of total flowpath length). Analysis of the data after accounting for dilution was performed by multiplying each flowpath by a dilution factor based on 1 g of material diluted by 5 min of 50 mm h^{-1} rainfall at 4-, 2.75-, 1.5-, 1-, and 0.5-m flowpaths (dilution factor = $0.9109 \times$ flowpath length$^{-1.2095}$). Once accounted for, the only consistent pattern in P loss for each fraction was evident for DURP in each soil (Berks low P soil, DURP = 19.04time$^{-1.13}$**; Berks high P soil, DURP-0.09 $\times$ time$^{1.14}$*; Watson low P soil, DURP = 0.0007time$^{2.69}$*; Watson high P soil, DURP = 0.98time$^{1.211}$*). Other significant relationships were noted, but these were not consistent among soil types or initial P concentrations and exhibited weak correlation coefficients (Berks low P soil, DRP = 10.43flowpath length$^{0.46}$*, TDP = 12.22flowpath length$^{0.41}$*; Watson low P soil, TDP = 8.68flowpath length$^{-0.37}$*, TDP = 1.05time$^{0.76}$**; Watson high P soil, TDP = 1.08time$^{0.77}$*). The relationship of DURP derived from manure with
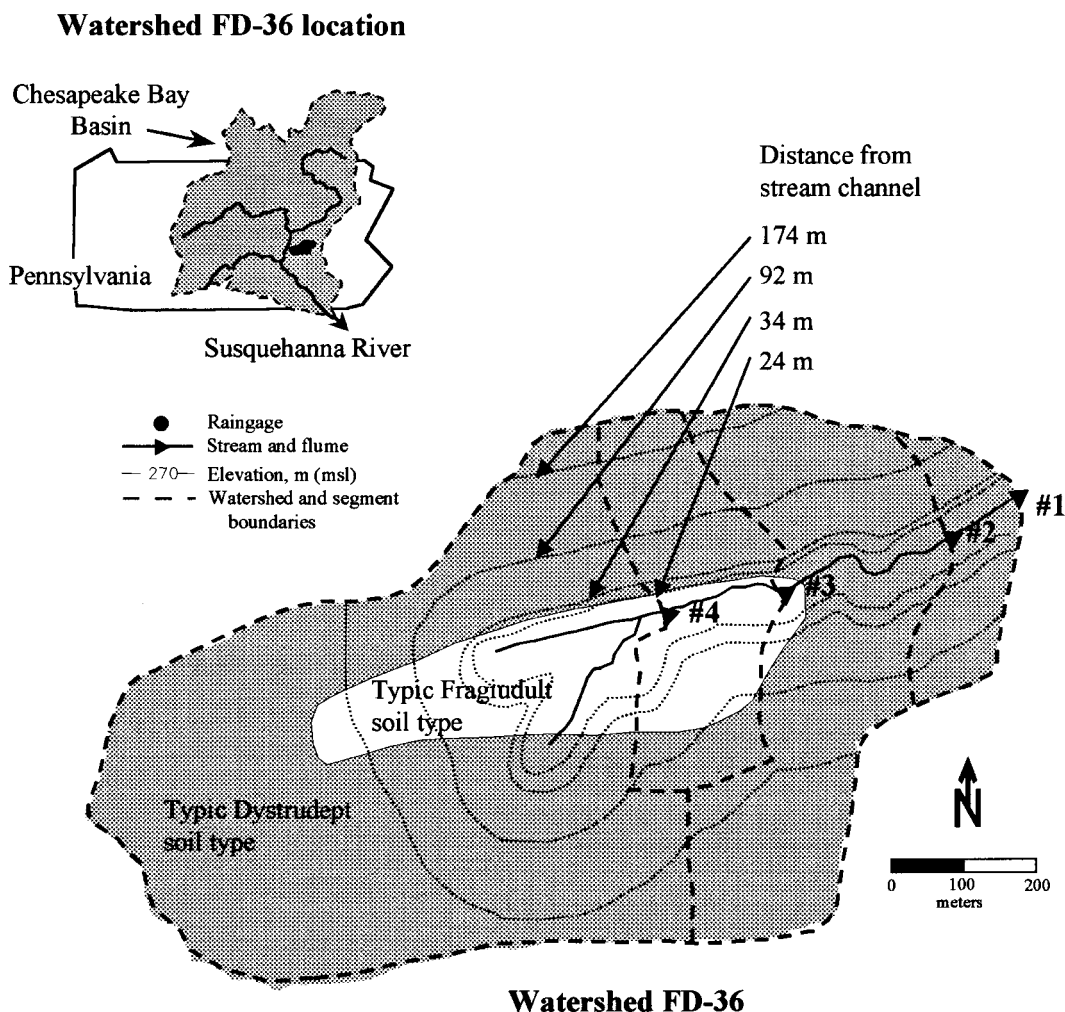

Watershed FD-36 location

Fig. 5. Soil types (Berks [Typic Dystrudept] and Watson [Typic Fragiudult]), segments (#1–4), and distance from the stream channel within the watershed FD-36.

time is again most likely a reflection of this fraction's increased solubility and mobility compared with the other fractions.

The absence of significant relationships between DRP and flowpath length (after dilution is taken into account) shows that little or no sorption of DRP by suspended sediments occurred during overland flow. The selective erosion of fine materials implies that suspended sediments may be a net sink for P (Kunishi et al., 1972; Sharpley et al., 1981b). However, this depends upon factors such as flow rate, the equilibrium phosphorus concentration (EPC, where the net influx of P is zero), and the sorption capacity of the sediments (House et al., 1995; House and Warwick, 1999). As EPC and sorption rate were not measured, the influence of P sorption during overland flow is unclear. However, House et al. (1995) predicted a decrease in P concentrations during flow of ca. 50% over a distance of 5000 m at a flow rate of 4.6 cm h^{-1} over sediments that contained a comparable concentration of total P (563 mg kg^{-1} compared with 540 mg kg^{-1} for the Watson low P soil; R.W. McDowell, unpublished data, 2000). If sorption was a factor in determining P in overland flow in response to a localized manure application, the P sorption effect would probably not be seen under the experimental conditions used here. Further research is required to confirm the role of soil or sediment sorption in determining overland flow P.

Perspective for Management within the Landscape

The present minimum concentration seen as likely to cause eutrophication in streams or other flowing waters not discharging directly into lakes or impoundments is 0.1 mg TP L^{-1} (Dodds et al., 1998; USEPA, 1994). Using the data presented in Table 3, it is possible to calculate the decrease of P with flowpath length, and when related to landscape position, where manure applications could be safely applied without exceeding 0.1 mg TP L^{-1}, if overland flow occurred. An example is given for the watershed FD-36 in central Pennsylvania, USA (where the soils originated). This watershed can be divided into subwatersheds, each of which is monitored for flow and P concentrations (Fig. 5). Data for the period from October 1996 to December 1999 indicated that a total of 110 events caused overland flow. By drawing a line across a hydrograph from the start of the event to the end of the event, overland flow can be separated from subsurface flow, and the volume of overland flow calculated from the area above the line. The volume of overland flow can then be divided by the length between each flume and the minimum distance required for saturation-excess overland flow can be calculated (Fig. 6).

Back-calculating from the TP equations given in Table 3 indicates that for a N-based manure application (equivalent to 75 kg P ha^{-1}, Sharpley and Beegle, 1999), the minimum distance from the stream channel required for TP concentrations in overland flow to be <0.1 mg TP L^{-1} ranged from 24 m in the Berks low P soil to 174 m in the Berks high P soil (Fig. 5). Distances for the Watson low P and high P soils were 34 m and 92

m, respectively. When the shortest distance (24 m for a Berks low P soil) is applied to the saturated distance from the stream channel, 13% of the overland flow events from October 1996 to December 1999 within Segment 1 would have contributed TP concentrations in excess of 0.1 mg L^{-1}, if manure had been applied. This decreased to 3% of overland flow events in Segment 4.

Using the next distance of 34 m for a Watson low P soil results in 8% of events within Segment 1 and <1% of events within Segment 4 in excess of 0.1 mg L^{-1} TP. However, when the location of each soil type is accounted for, the numbers of contributing events in excess of recommended guidelines change. This is evident in Fig. 5 for Segments 3 and 4, where the dominance of the Watson soil type near the stream channel implies that fewer events will contribute to eutrophic concentrations of P in streamflow. However, what is clearly evident from Table 3, and the resultant calculations of minimal safe distance from the stream channel, is the dependence of TP concentrations on the initial soil P concentration. Consequently, while we have identified dilution and physical processes as significant controlling influences on the P dynamics in overland flow, the P concentration of the soil should not be discounted when looking at contributing areas of P loss within a watershed.

We remind the reader that within a landscape, overland flow represents both a source and sink for P loss by initiating and stopping transport. While our data represent an idealized condition (i.e., continuous saturation-excess overland flow), Fig. 6 shows that saturation-excess overland flow could occur up to 80 m from the stream channel. Thus, our data would suggest that any application of manure within this distance would represent a source of P export. This has been recognized in
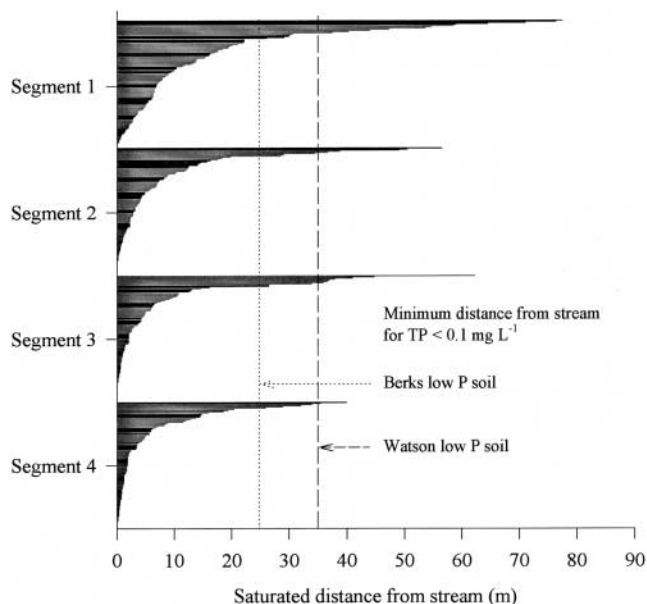

Fig. 6. Saturated distance from stream in each of the four segments (Fig. 5) within the FD-36 watershed for storms producing overland flow from October 1996 to December 1999 ($n = 110$). Dotted line represents minimum distance from the stream for total phosphorus (TP) concentrations < 0.1 mg L^{-1} for Berks low P soil (......) and Watson low P soil (------).

recent work linking P sources and transport mechanisms to minimize P loss in tools such as the "P index" to P management, which identifies these areas as critical source areas of P loss (Gburek et al., 2000; McDowell et al., 2001b).

CONCLUSIONS

Data show that the quantity–intensity relationship that exists between Mehlich-3 extractable P and water-extractable P of soils is also evident between Mehlich-3 extractable P from sediments and DRP in overland flow. The concentration of DRP in overland flow may be more accurately estimated by a water extraction of sediments at sediment to solution ratios similar to those found in overland flow. Once overland flow began on an untreated soil, P concentrations of most fractions decreased with time, except DURP, which increased. This was attributed to a combination of slaking, dispersion, and the preferential erosion of fine particles of high P content. A relationship was found between the proportion of clay in the sediment and the DRP concentration of overland flow. After soils were manured, the effect of slaking and dispersion on P decreased, as did the strength of the relationship between DRP in overland flow and the proportion of clay in sediment. However, the strength of the relationship to the proportion of larger (sand-sized) particles increased and was attributed to manure application and the rollover of larger, lower-density particles as flocs.

After manuring, no consistent relationship was found between the concentration of P fractions in overland flow and the duration of the event. However, a strong relationship was found between P fractions and flow-path length. Further analysis indicated that the decrease in the concentrations of all P fractions was unlikely to be caused by sorption or retention of P by the soil and that dilution probably was the controlling factor influencing P dynamics in response to a localized manure application.

Large differences were noted in P losses between the two soil types, one (the Watson soil) losing more than twice the total P (largely in the form of particulate P) as the other irrespective of their extractable P content. In addition, differences in P losses were noted within a soil type depending upon the initial P concentration of the soil, even in the manured soils. Hence, while there was a significant effect of duration of an overland flow event in an unmanured soil and dilution in a soil with a localized manure application, soil P concentrations should not be discounted when looking at the landscape for potential areas of P loss via saturation-excess overland flow within a watershed.

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Organic Compounds in the Environment

Sensitivity and First-Step Uncertainty Analyses for the Preferential Flow Model MACRO

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ABSTRACT

Sensitivity analyses for the preferential flow model MACRO were carried out using one-at-a-time and Monte Carlo sampling approaches. Four different scenarios were generated by simulating leaching to depth of two hypothetical pesticides in a sandy loam and a more structured clay loam soil. Sensitivity of the model was assessed using the predictions for accumulated water percolated at a 1-m depth and accumulated pesticide losses in percolation. Results for simulated percolation were similar for the two soils. Predictions of water volumes percolated were found to be only marginally affected by changes in input parameters and the most influential parameter was the water content defining the boundary between micropores and macropores in this dual-porosity model. In contrast, predictions of pesticide losses were found to be dependent on the scenarios considered and to be significantly affected by variations in input parameters. In most scenarios, predictions for pesticide losses by MACRO were most influenced by parameters related to sorption and degradation. Under specific circumstances, pesticide losses can be largely affected by changes in hydrological properties of the soil. Since parameters were varied within ranges that approximated their uncertainty, a first-step assessment of uncertainty for the predictions of pesticide losses was possible. Large uncertainties in the predictions were reported, although these are likely to have been overestimated by considering a large number of input parameters in the exercise. It appears desirable that a probabilistic framework accounting for uncertainty is integrated into the estimation of pesticide exposure for regulatory purposes.

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$\mathbf{M}$UCH attention has focused on the role of preferential flow in mediating pesticide leaching through soil. There is wide evidence to demonstrate that preferential flow occurs in soils of varying texture (Beven and Germann, 1982; Brown et al., 1995). Preferential flow may result from the presence of macropores (shrinkage cracks and fissures, soil fauna channels, root holes) in structured soils (Beven and Germann, 1982), but also from profile heterogeneities (e.g., horizon boundaries) or water repellency (Hendrickx et al., 1993) in unstructured sandy soils. Relatively rapid movement of water through only a portion of the bulk soil may significantly increase chemical transport by bypassing the soil matrix and decreasing residence time in the upper soil layers where sorption and degradation are generally most important (Brown et al., 2000b). A number of mathematical models have been developed to simulate the transfer of water and solutes in soil resulting from preferential flow phenomena (e.g., Ahuja et al., 1993; Hall, 1993). To date, one of the most widely used is the dual-porosity model MACRO, which divides the soil into micropore and macropore regions (Jarvis, 1994). The model can be set up to simulate a soil where the hydrology is dominated by preferential flow, a soil with no preferential flow at all, or any combination of flow types between these two extremes. MACRO has been used to simulate